

Ch 14
(297/1961)

UDC 536.662:662.641

ACTA POLYTECHNICA SCANDINAVICA

CHEMISTRY INCLUDING METALLURGY SERIES No. 14

STIG SUNNER and INGEMAR WADSO

**Measurements on Heat Effects Accompanying the
Wet Carbonization of Peat in the Temperature
Range 20 to 220 Degrees C**

Swedish Contribution No. 13
STOCKHOLM 1961

ACTA POLYTECHNICA SCANDINAVICA

... a Scandinavian contribution to international engineering sciences

Published under the auspices of the Scandinavian Council for Applied Research

in *Denmark* by the Danish Academy of Technical Sciences

in *Finland* by the Finnish Academy of Technical Sciences, the Swedish Academy of Engineering Sciences in Finland, and the State Institute for Technical Research

in *Norway* by the Norwegian Academy of Technical Science and the Royal Norwegian Council for Scientific and Industrial Research

in *Sweden* by the Royal Swedish Academy of Engineering Sciences, the Swedish Natural Science Research Council, and the Swedish Technical Research Council

Acta Polytechnica Scandinavica consists of the following sub-series:

Chemistry including Metallurgy Series, Ch

Civil Engineering and Building Construction Series, Ci

Electrical Engineering Series, El

Mathematics and Computing Machinery Series, Ma

Mechanical Engineering Series, Me

Physics including Nucleonics Series, Ph

For subscription to the complete series or to one or more of the sub-series and for purchase of single copies, please write to

ACTA POLYTECHNICA SCANDINAVICA PUBLISHING OFFICE

Box 5073
Stockholm 5

Phone 67 09 10

This issue is published by
THE ROYAL SWEDISH ACADEMY OF ENGINEERING SCIENCES
Stockholm, Sweden



Measurements on Heat Effects Accompanying the Wet
Carbonization of Peat in the Temperature Range 20 to 220 Degrees C

by
Stig Sunner and Ingemar Wadsö
Termochemistry Laboratory
Lund University
Lund

ACTA POLYTECHNICA SCANDINAVICA
CHEMISTRY INCLUDING METALLURGY SERIES No. 14
(AP 297 1961)

CONTENTS

	Page
INTRODUCTION	3
GENERAL CONSIDERATIONS	4
PRELIMINARY INVESTIGATIONS	11
APPARATUS	13
EXPERIMENTAL PROCEDURE	19
CALCULATION OF RESULTS	23
MATERIALS	25
CALORIMETRIC RESULTS	26
ESTIMATION OF THE ENTHALPY CHANGE	29
DISCUSSION OF RESULTS	34
ACKNOWLEDGEMENTS	39
REFERENCES	40

INTRODUCTION

Since 1850, when the first patent was issued on a wet-carbonization process for peat¹, much work has been devoted to the study of this method. For an evaluation of the economy of the process it seems to be of crucial importance to know the sign and magnitude of thermal effects accompanying the heating of a peat suspension from room temperature up to 200-250°C. This question has also received considerable interest and a number of investigations has been reported on the subject^{2, 3, 4, 5, 6}. Only Lundén and Cederquist⁶ have gone to the trouble of measuring the heat effects calorimetrically. The results obtained by these authors indicate an exothermicity of 50 to 150 kcal/kg d.wt.*) in the temperature range 20-180°C.

Odén² and Odén and Unnerstad³ have estimated the heat effects indirectly by determination of heats of combustion of the peat prior to and after heating to 225°C. For sphagnum peat they obtain values of ca. 1000 kcal/kg d.wt. and for other types considerably smaller values. Terres⁴ and Terres and Schultze⁵, who probably have used the same method, also find a considerable exothermicity and give values of ca. 500 kcal/kg d.wt. for a heat treatment between room temperature and 265-300°C.

On the other hand, Widell⁷, who used almost dry peat (2-10 % of water) and a qualitative thermal analysis method⁸, reaches the conclusion that the sum of the heat effects are endothermic below 225°C.

A critical examination of the given references strongly indicates that the only reasonably reliable data are those given by Lundén and Cederquist. However, the conditions under which these data were obtained differ appreciably from those considered to be optimal for an industrial process. The measurements must be extended to 200-220°C and the rate of heating should be as fast as possible. Further, it seems fairly well established that different kinds of peat behave differently during the heat-treatment. It is therefore desirable to measure the same kinds of peat which are considered as raw materials in an industrial wet-carbonization process and also to characterize the samples botanically as well as from the standpoint of degree of humification.

These considerations governed the decision to undertake a calorimetric study of the process under conditions closely similar to those under which AB Svensk Torvförädling will operate a plant under construction.

*) dry weight

GENERAL CONSIDERATIONS

Defining the problem

In order to be of a scientific value, the experimental measurement of a heat quantity liberated or absorbed during a process must be related to well-defined initial and final states. Rigorously, this means that the chemical and physical changes occurring during the reaction must be well-known and quantitatively evaluated.

Already, from the fact that peat itself is an extremely complex and unanalyzable mixture of unknown chemical species kept together in a state which cannot be physically defined, it is clear that a rigorous treatment of the present problem can never be achieved and thus the results obtained will be of small - if any - scientific value.

Primarily, the goal of the present investigation has been to gain knowledge of the heat effects occurring during the technical wet-carbonization process as carried out under certain specified conditions. The following questions arise: Firstly, is this at all possible in laboratory experiments and, if so, how shall the experiments be performed to get the best technically useful results out of them?

The first question is related to the possibility of obtaining reproducible samples. Although peat is undefinable, a certain source of peat may, on average, be of such a constant composition and state as to allow taking a reliable master sample. After homogenizing, experiments performed on this batch may be representative for the whole deposit of peat.

As the composition of the peat may vary from place to place even within the same deposit, several master samples must be prepared and investigated under the assumption that the sampling procedure is adequate.

The second question means that experiments have to be designed in such a way as to simulate closely the industrial procedure. However, differences are unavoidable and it is therefore necessary to specify the chemical and physical conditions under which the reaction takes place. In order to do this the gross changes during the process must be examined.

Chemical reactions of many kinds occur during the warm-up of a peat suspension. This is evident from the fact that the dry weight of the insoluble material diminishes by 30 to 35 %. Roughly 10-15 % of the initial weight is transferred into water and volatile compounds, 10 % into carbon dioxide and 10 % into water soluble products. It is suggestive that the low molecular weight products of decomposition can be traced back to a removal of oxygen, mainly in carboxylic and hydroxylic groups, both of which are strongly hydrophilic. In the liquid phase dissolved air may play a certain role for oxidative degradations.

The physical changes occurring during the heating concern mainly the carbon dioxide formed and the vaporization of water. When the process is carried out in a closed system three different phases must be considered - the solid 'peat', the water solution, and the gas phase. The carbon dioxide will be distributed between the different phases and the amount of water vapor is dependent on the gas phase volume, on the amount of dissolved substance in the liquid phase, and on the carbon dioxide pressure in the gas phase.

All the chemical and physical processes are accompanied by heat effects, i.e. changes in the total energy of the system. By far the largest energy quantity involved, however, is the amount supplied for heating the water and vaporizing part of it in order to reach equilibrium. In a 5 % peat suspension the energy required to heat 1 kg from 20° to 220° (including a normal vaporization) is ca. 20 Mcal., whereas the "exothermicity" of the process is less than 50 kcal. The "corrections" necessary to apply to arrive at the net from the gross heat effect are thus 400 to 1000 times as large as the net heat effect itself. A very modest precision of, say, 20 % in the determination of the heat effect thus requires an over all precision in the calorimetric measurement in the order of 0.05 %. This cannot be achieved without using some kind of a reference system, which preferably should be easily defined, both chemically as well as physically. The choice of reference system must also be governed with respect to the type of information that is needed in planning the industrial process. The actual situation may be analyzed in the following way.

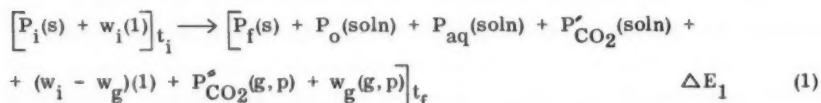
The measurement of the increase in internal energy of a peat suspension, being heated from 20° (t_i) to t_f °C may be carried out in a closed system, e.g. calorimetric bomb. In a measuring experiment an amount of, say, 5 % peat suspension is introduced into the bomb. *) The initial state at t_i °C then consists of the peat suspension and a gas phase of nitrogen and saturated water vapor at 1 atm. pressure.

*) The suspension should be in equilibrium with air in order to simulate the conditions of the technical process.

The final state at $t_f^{\circ}\text{C}$ consists of the carbonized peat suspension (ca. 3.5 %) in a dilute aqueous solution of low-molecular weight organic matter, like formic acid and carbohydrates. The actual amount of soluble material is ca. 0.5 %. The volume of the liquid phase has increased considerably due to the decreased density of the water phase at the high temperature. The gas phase now consists of nitrogen, water vapor at several atmospheres pressure, and released carbon dioxide, the amount of which is ca. 0.5 % by weight.

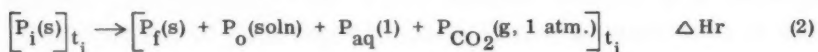
Let P_i stand for a unit quantity dry weight of solid native peat in equilibrium with liquid water, let the reaction products from P_i be carbonized peat, P_f , water soluble materials, P_o , water, P_{aq} , and carbon dioxide, P_{CO_2} . The total amounts of water present in the initial and final states are w_i and w_f , respectively, and the vaporized water at t_f amounts to w_g . The total pressure in the gas phase is p and the partial pressures are P_{aq} and P_{CO_2} for water and carbon dioxide, respectively.

Then, the reaction can be described by the following equation:



ΔE_1 stands for the total increase in internal energy of the system.

Before going on to the comparison experiment we must define the expression "exothermicity of the wet-carbonization process". According to the practice in defining heats of reaction we may write the isothermal process occurring at $t^{\circ}\text{C}$ and 1 atm. as

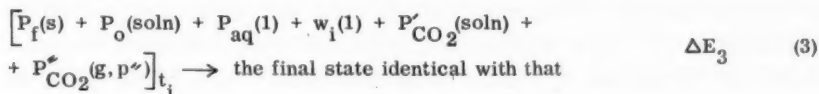


ΔH_r is the enthalpy increase during the reaction.

It must be emphasized that the reaction, thus written, represents a hypothetical case - the complex sequence of reactions behind the above equation does not occur at a certain temperature but rather within one or several fairly broad temperature intervals.

The heat of wet-carbonization of peat, thus defined, can be evaluated by performing a reference measurement on the final state mixture from the main experiment. The calorimetric bomb has simply to be cooled down to $t_i^{\circ}\text{C}$ and the measurement repeated between the same temperature limits.

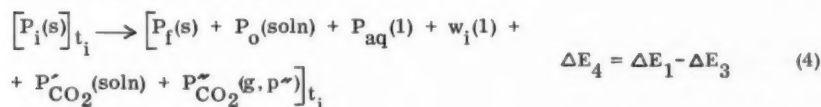
Provided no further reaction takes place during the second heating period, the reference experiment can be described by



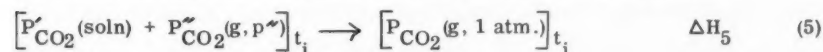
of equation 1,

where P'_{CO_2} and P''_{CO_2} are the amounts of carbon dioxide in solution and in the gaseous phase, respectively, and p^* is the total pressure above the solution. ΔE_3 is the change in internal energy accompanying the process.

Subtracting (3) from (1) gives:



By applying corrections for the heat of vaporization of the dissolved amount of carbon dioxide and the heat of expansion of the gaseous carbon dioxide,



the isothermal heat of wet-carbonization is obtained as

$$\Delta H_r = \Delta E_1 - \Delta E_3 + \Delta H_5$$

The standard procedure described is capable of giving information on the heat of reaction at a reference temperature, in this case at the starting temperature, say, 20°C. As was pointed out, this result refers only to the hypothetical isothermal reaction which is of fundamental importance when treating well-defined reactions and systems. The problem of industrial interest, however, is rather different and can be stated as: What are the integral and differential energy requirements to heat up a given peat suspension from, say, 20°C to 220°C? That is, at what temperature intervals do the wet-carbonization reactions occur as judged from the measured changes in internal energy?

If the two experiments are performed under identical conditions, a recording of the heating curves between t_i and t_f can be used for the calculation of ΔH_r at any intermediate temperature, provided the heat capacities of the reactant and the reaction products are known together with their variation with temperature. The complex and mostly unknown nature of the chemical constituents of the system makes a rigorous calculation impossible and the best that can be done is a very rough estimation. Lundén and Cederquist⁶ used this method and simply put the heat equivalent

of the native peat equal to that of its decomposition products at all stages of the wet-carbonization process. Even though it can be expected that the heat equivalent of the reaction products is significantly higher than that of the native peat (due to the formation of ca. 10 % of water), it is a reasonable approximation, introducing a possible error in the heat of reaction value of perhaps, 6 kcal. per kg peat d. wt.

Another source of error which is caused by the complex nature of the liquid phase in the comparison experiment, depends on the presence of carbon dioxide in the reference system from the very start of the experiment. The amount of CO_2 dissolved escapes the solution in a temperature region below that where CO_2 is formed during the wet-carbonization. If about 70 % of the CO_2 vaporizes, the corresponding heat of vaporization under the given conditions amounts to ca. 7 kcal. per kg of peat d. wt.

The influence of other reaction products is unknown and, thus, the complex nature of the carbonized peat suspension makes it unsuitable to be used as a reference system if the thermal behaviour of the native peat has to be studied in a broad temperature region.

The given considerations have governed the choice of pure, distilled water to be used in the reference system. In that way, the heat quantity supplied to heat a given amount of peat suspension from one temperature to another can be related to the well-known heat quantity that has to be transferred to the same amount of water in order to affect the same temperature change.

It is evident, that by this choice, the isothermal heat of wet-carbonization as defined by equation (2) cannot be found without the application of a number of corrections. However, the experimental approach is more directed towards obtaining information useful for the planning of an industrial process.

Experimental approach

The methodological features that had to be considered in designing the calorimetric apparatus were partly unique and presented a number of constructional difficulties.

The unusually wide temperature span of the experiment, 20 to 220°C, makes it necessary to work with an adiabatic calorimeter in order to minimize heat exchange errors. Even so, the high heating rate, 5-10°C per minute, causes unavoidable temperature differences both on the outer surface of the bomb as well as on the inner surface of the surrounding jacket, facing the bomb. As the heat transfer (con-

duction, convection and radiation) is caused by the temperature difference between these two surfaces, it varies between different parts of the system, which means irregular heat leakage. Due to limited heat transfer within the bomb and jacket, the localized temperature measuring device will indicate a temperature which is different from that of the corresponding surface during the heating period. This effect also causes a systematic error which cannot be accounted for.

Considering the rather high precision aimed at, ca. 0.05 %, in order to get the desired heat of carbonization value with an accuracy of ± 20 %, the heat exchange errors may easily be significant, in fact they can overshadow the fraction of the heat of carbonization which is given of (or adsorbed) in a certain temperature interval.

It was therefore decided to build a twin-calorimeter in which the two experiments are carried out simultaneously under as nearly identical conditions as possible. If the two bombs are placed within a surrounding mantle in such a way as to assure a stable and bisymmetrical geometry of the system, the heat exchange errors will largely cancel. However, small differences will remain from the different thermal behaviour of the two liquid phases. In the bomb, charged with native peat, the heat conductivity of the suspension is, at least at fairly low temperatures, lower than that of the reference liquid, water, probably due to higher viscosity. This will give rise to a temperature difference between the outer surfaces of the bombs and thus, a difference in heat exchange with the surroundings. Further, during the very rapid heating period it is in practice impossible to compensate in the reference system for the heat effects which occur in the peat suspension.

From what has been said it is evident that heat conductivity and transfer problems must be carefully considered. The distribution of the electrical energy from the heater to the whole calorimetric bomb must be as rapid and even as possible, and that for two reasons. Firstly, the risk for charring some peat on the metal tube surrounding the heater is obvious and must be prevented because of the accompanying heat effects as well as of the resulting decrease in heat transfer between the heater and the liquid phase. Secondly, a slow and uneven distribution of the heat causes the temperature differences on the outer surface of the bomb to increase and the heat exchange with the jacket becomes more irregular and difficult to control or estimate.

The heat equalization can be facilitated in a number of ways. The liquid must be thoroughly stirred, which is preferably achieved by a rotation of the calorimeter bombs. (Cf. Ref. 6). In order to speed up the heat transfer from the centrally

placed heater to the liquid, the heater tube should be equipped with axial flanges⁶, which also makes the stirring more efficient. One factor which is of considerable importance is the design of, and the construction material used for, the calorimeter bomb. Stainless steel is a bad thermal conductor and should not be used in constructions where the lid and its closing mechanism must be made of heavy material. For these reasons brass was chosen as the construction material in the final version of the calorimeter bombs. Further, the use of a lid was avoided and the bombs were simply closed by screws equipped with lead gaskets.

PRELIMINARY INVESTIGATIONS

The investigations reported in this paper were preceded by a rather long development phase during which three different types of calorimeters were built and tested. The essential experience gained from this work will be shortly described.

Stainless steel is the obvious construction material for the calorimeter bombs and was used in the beginning. It was found, however, that the low thermal conductivity of the steel seriously increased the time of equilibration particularly at high heating rates. When the bomb had a conventional type of head with a lid fastened by bolts and screw nuts, this difficulty was very pronounced. It was therefore decided to use brass instead of steel. The heat conductivity of brass is 2 to 6 times as large as that of steel. The less favorable mechanical properties must be taken into account, but no serious problems are met within the pressure and temperature regions of interest in this work. Different parts of the bomb could easily be soldered together by use of silver alloys with different hardening temperatures. Inside corrosion had to be prevented by electrolytic plating. The best metal seems to be silver as it precipitates without pores and in a smooth coating, even if the cathodic surface (i.e. inner surface of the bomb) is rather complex. The silver layer was found to withstand corrosion from the acidic bomb solution during the experimental conditions.

The leakage problem has been given due consideration. Even a fairly small leak causes an escape of water vapor which energetically completely overshadows any thermal effect from the wet-carbonization reactions. The difficulty has been to combine the need for a light-weight construction of the head of the bomb with the necessity of a safe and tight seal during the rapid heating, which introduces serious thermal strain into the different parts of the bomb. A number of designs have been tested with gaskets (O-rings, cuffs) of different materials, like silicone rubber, teflon, aluminium, and lead. It was concluded that metal gaskets were superior to those made of organic materials, under operating conditions. Further, it was found that the two given requirements could not both be fulfilled if the diameter of the lid should approximately equal that of the body of the bomb. Either, the disadvantage of a heavy head must be taken, or that of a small opening, and the latter was finally chosen.

The mutual location of the wells for the heater and the resistance thermometer has been especially studied. In a rotating bomb the heater should be placed centrally to assure symmetric flow of heat. The temperature may be measured in the bomb liquid or in the bomb wall. Principally, as the most important error is due to heat transfer, the temperature should be measured as close to the bomb surface as possible and, thus, the well for the thermometer should be drilled in the bomb body. Experiments with a steel bomb equipped with a thermometer well placed in the middle of the free space between the heater tube surface and the inner surface of the bomb body showed a rather unexpected result: When native peat was used and the rate of heating was 5°C per minute, the temperature in the bomb liquid was found to be ca. 10° higher than that of the bomb wall.

A problem which caused much trouble was the design of the heating element with the high effect necessary to use in order to attain an appropriate heating rate, the resistance wire tends to become too hot which affects the resistance and the lifetime of the heater.

Commercially available heating elements of the hermetically sealed type were tested and found unsuitable. Other designs, where the resistance wire was embedded in insulating powders, were also rejected. The construction which was found satisfactory had a more freely suspended resistance wire and will be described later.

Several types of flanges were made and tested for efficiency of stirring and heat conductivity. The tests showed that axial flanges machined together with the heater well out of one solid piece of brass gave the best results. Systems consisting of flanges welded or soldered to one or several pieces of metal tubing snugly fitting on the heater tube showed a much less favorable heat conductivity and often gave rise to charring in small cavities between the different parts.

APPARATUS

Calorimetric equipment

The complete calorimetric apparatus, illustrated in Figure 1 a to c, consists of two identical calorimeter cans (bombs) made of brass, a surrounding air thermostat, and a motor with transmission for bringing about the rotation of the bombs within the thermostat.

Figure 2 shows cross-sections of the bomb, parallel (a) and perpendicular (b) to the bomb axis. The bomb consists of three main parts: The bottom, A, with the axial tube for the heater and six flanges (machined from one piece of metal); the cylinder wall, B, with the wells for two platinum resistance thermometers; and the cover, C, with stainless steel linings, E, for the brass bolts, D. The different parts were soldered together using silver solders of different melting points. The distribution of mass is approximately symmetric, the bottom and top parts having about the same weight. The total bomb weight is 3.5 kg, the same within 3 g for the two bombs. The inner free volume is 520 ml. The bombs were designed for safe operation at 30 atm. pressure and 230°C.

The heating element was built round a central tube of ceramic, F, Figure 2. Two steel plates, G, were cemented to the tube and provided with 8 holes, in which thin-walled tubes of ceramic, H, were fastened by cementing. A spiral made of 0.4 mm Kanthal wire (total resistance ca. 70 ohms) was inserted into the tubes. The ends of the wire were welded to copper-wires which passed out from the bomb through a steel washer, acting as a shield, rockwool, and a plug of teflon. The leads to the heater were insulated by woven glassfiber tubings. The heat capacity of the element was found to be very small and after 20 hours of continuous operation at full load the resistance (at a given temperature) did not change significantly during a full series of experiments.

The two 100 ohms resistance thermometers were connected in series, and the leads were insulated by teflon tubings.

The bomb was filled, cleaned and emptied through the two steel-lined holes, diam. 15 mm., in the top cover, C, Fig. 2 a. The bolts, D, have a sharp rim on the heads that acts on a lead gasket placed in a groove in the cover. With this construction leak problems were successfully overcome.

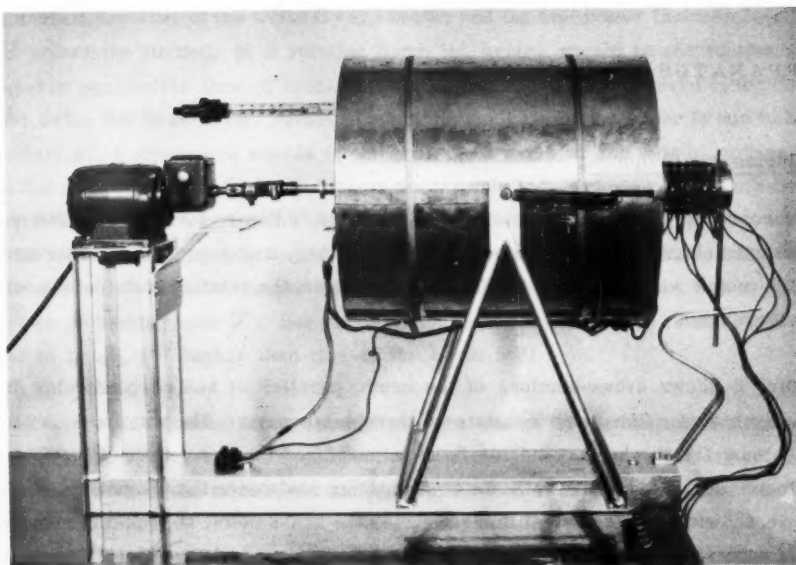


Figure 1 a

The exterior of the calorimetric set-up with the motor connected to the rotation shaft of the calorimeter. The thermostat is hung up between trestles and can easily be tilted through 90° into a vertical position. The slip ring assembly is seen at the right.

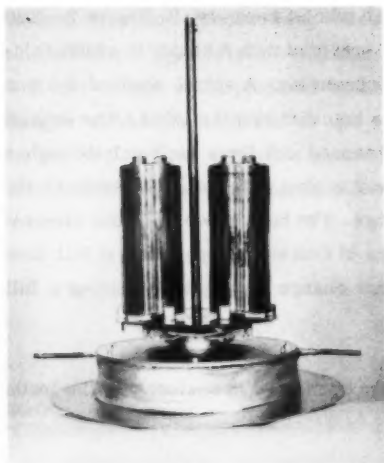


Figure 1 b

The dismantled calorimeter fixed to the cover of the thermostat through the central axis of rotation.

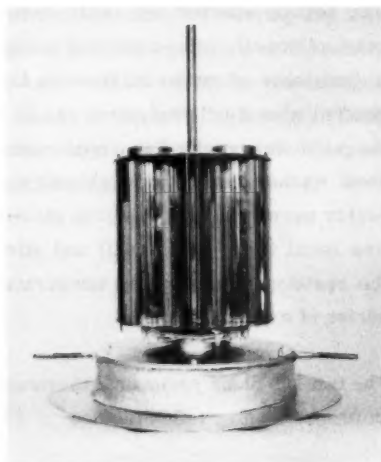


Figure 1 c

The radiation shields are removed showing the two bombs supported by the teflon bolts.

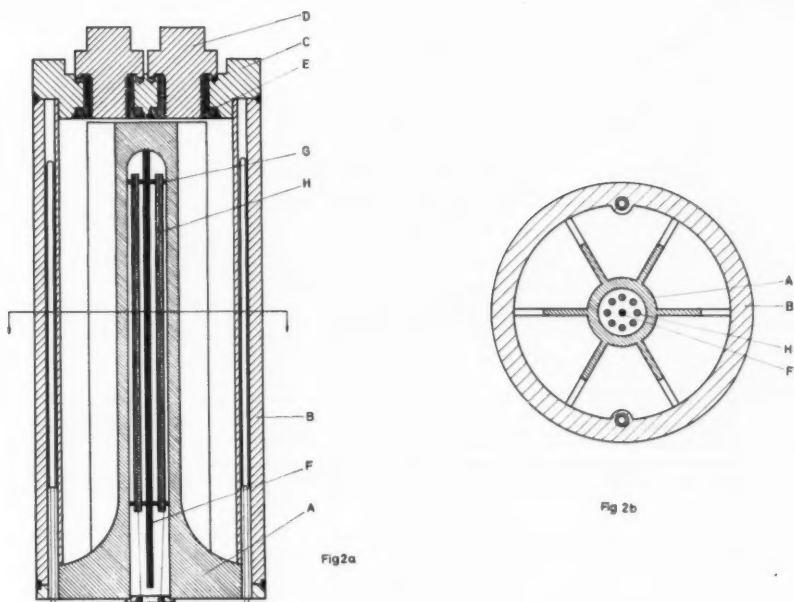


Figure 2 a - b

Cross-sections of the bomb, parallel to (a) and perpendicular to (b) the bomb axis. For explanation see the text.

The time of equilibration for this bomb was found to be 3 minutes which should be compared to the value of 15 minutes determined for a conventional steel bomb of the same size.

The two calorimeter bombs, F, Figure 3, are held in place between brass shields, H, by means of shaped teflon bolts, G, 3 at each end. A thin-walled brass cylinder, E, serves as a shield to diminish heat leakage. Both the brass shields, H, and the cylinders, E, have highly polished, chromium-plated surfaces. The electric leads from the bombs were carried out to the slip ring assembly, L, through the hollow axis of rotation, I. For the sake of simplicity the hitherto described parts, the bombs with shields mounted on the shaft of rotation, will be called "the calorimeter".

The calorimeter is placed in an air bath consisting of a drum, C, made of 5 mm iron plate, with lid, K, (Fig. 3) covered with mica and wound all over with 1 mm Kanthal wire. The bath could either be kept at a constant temperature by use of a mercury contact thermometer, D, or it could be operated to follow closely the temperature changes of the calorimeter bombs. The iron drum is insulated with a 50 mm layer of rockwool, B, covered by a 1 mm aluminium plate, A.

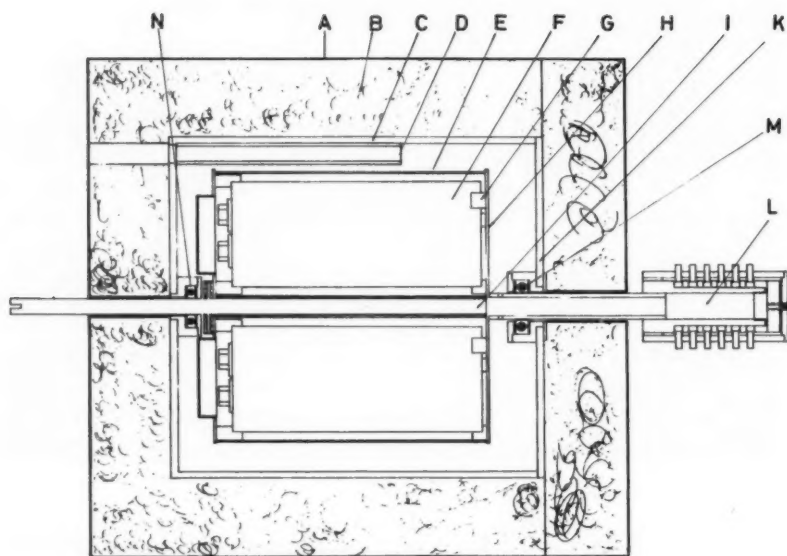


Figure 3

Cross-section of the thermostat with inserted calorimeter.
For explanation see the text.

The calorimeter axis is supported by two ball-bearings, M and N (Fig. 3). M is driven on the axis and, thus, the calorimeter is permanently connected to the lid of the thermostat. The opposite end of the axis passes through N and is fixed to the ball-bearing by use of an expanding clutch (seen on Fig. 1 a to the left of the thermostat). The lid of the thermostat is kept in place by two springs (Fig. 1 a).

The rotation, 11 r.p.m., is achieved by means of a motor with gear-box (Fig. 1 a) flexibly connected to the shaft of the calorimeter. The whole system is mounted on trestles and can be moved on a channel bar (Fig. 1 a).

The slip ring assembly consists of a nylon drum on which six copper rings have been driven. On an outer nylon drum are mounted six pairs of brushes made of bronze carbon pressed towards the copper rings by springs. The contact resistance was found to be negligible.

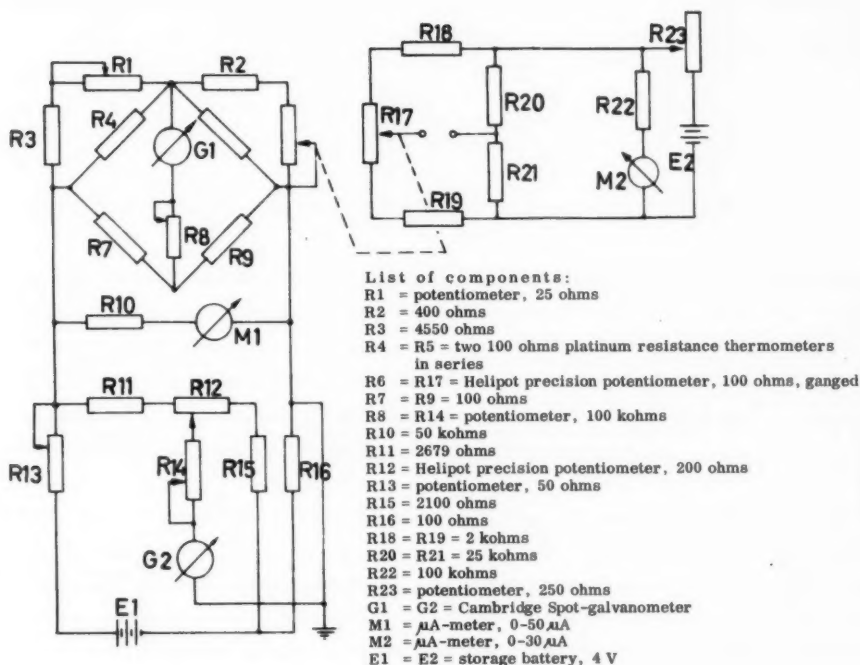


Figure 4. Circuit diagram of the temperature measuring system.

Electrical equipment

The temperature measuring system is shown in Figure 4. The two platinum resistance thermometers in each calorimeter are connected in series (R4 and R5) and are part of a Wheatstone bridge. Once the bridge is balanced with the resistance thermometers at the same temperature, it is balanced in the whole temperature region. A small temperature difference is compensated with one of the ganged Helipot precision potentiometers R6 and R17. By watching the Spot galvanometer G1 set at zero the position of the Helipot continuously shows the temperature difference between the two bombs. R17 is part of a potentiometer circuit that feeds a Varian recorder, which records the temperature difference.

As the thermometer resistances change the current through the bridge and resistances R13 and R16, in series, will change. The voltage from the storage battery is, within narrow limits, constant and, thus, the potential across R16 depends on the average temperature of the thermometers and is determined by a compensation method (circuit R15, R12 /precision potentiometer/, R11, and R13). When the galvanometer G2 is at zero, the value read on R12 gives directly the mean temperature of the two bombs.

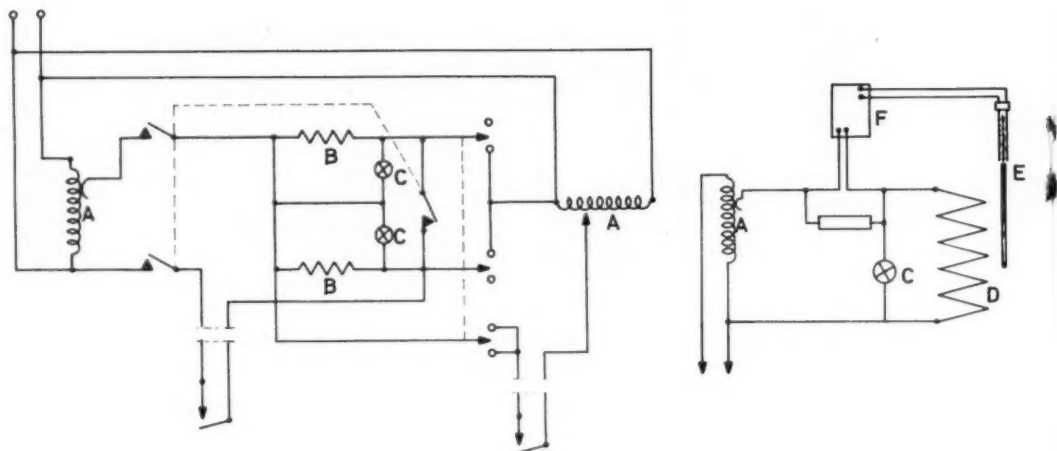


Figure 5 a - b

Circuit diagram for the calorimeter (a) and thermostat (b) heaters
A variable transformers, B calorimeter heaters, C signal lamps,
D thermostat heater, E mercury contact thermometer, F electronic
power relay.

The calorimeter heaters and the thermostat were fed from the AC mains through variable transformers (Figure 5). The voltage was constant only to ca. $\pm 2\%$ and was controlled with a calibrated voltmeter, accuracy $\pm 1\%$. The reason why no measures were taken to increase the precision was simply that in the strictly comparative measurement the large quantities of electric energy evolved in the bombs were identical and only the difference added at the end of the heating period to one of the bombs will suffer from the uncertainty, which is estimated to $\pm 3\%$ totally. The voltage over the thermostat resistance was so adjusted that the increase in the temperature of the thermostat followed that of the calorimeter.

EXPERIMENTAL PROCEDURE

The procedure followed in the present investigation was to make two series of experiments on each sample of peat. One series in which the temperature was raised stepwise, approximately in the intervals 20, 40, 70, 100, 130, 160, 190, and finally to 220°C and to equilibrate the system between the heating periods. A second series of measurements was performed by continuous heating between 20 and 220°C. Control experiments were made frequently with water in both bombs.

The dry, weighed bombs were filled with 350.00 ± 0.02 g of peat suspension or water, and closed. The calorimeter was assembled and inserted in the thermostat. After equilibration at 20°C the heating was simultaneously started in the bombs and in the thermostat. The setting of the variable transformer output voltages were such as to assure an equal rise in temperature of the calorimeter and the airbath to within $\pm 2^\circ\text{C}$. In the continuous heating experiments the power was switched off when the recorded temperature was 198°C, calorimeter and thermostat then both reached the final temperature 220°C. Meanwhile, the thermostat control was switched on and kept the air bath constantly at 220°C. The Helipot potentiometer R6 was manually operated so that the temperature difference between the two bombs could be recorded and readings of the setting of R12 were taken at constant time intervals in order to record the mean temperature of the two bombs. When the temperature difference between the bombs had been established, additional energy was fed into the coolest bomb until the difference in temperature was zero.

In the stepwise experiments the heating was switched off at 37, 64, 91, 118, 145, 171, and 198°C in order to reach the final temperatures 40, 70, 100, 130, 160, 190, and 220°C, respectively.

The recordings from a series of experiment are illustrated in Figure 6; curve a shows a control experiment, b a stepwise, and c a continuous experiment. From curve a it is evident that the two bombs are not operating under precisely identical conditions, and this deviation mainly concerns the equilibration. The determined temperature difference decreases rapidly to almost zero when the power is switched off. The small amounts of excess energy supplied to the coolest bomb to reach zero temperature difference were applied as corrections in the main experiments.

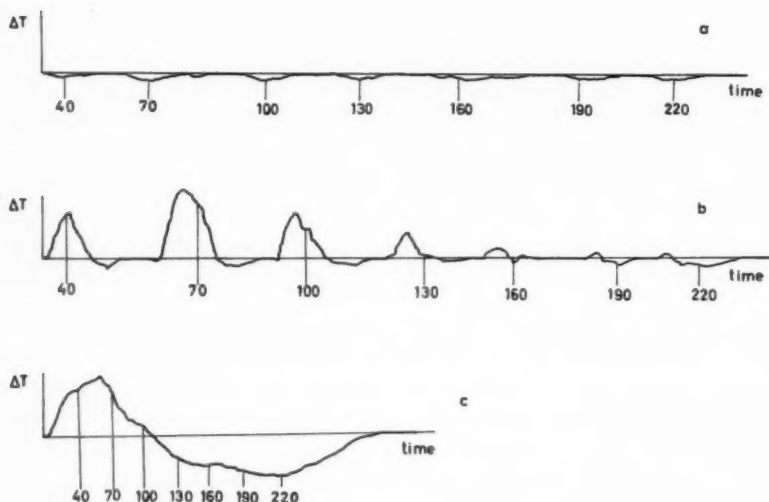


Figure 6

Indicated temperature difference between the two bombs as a function of time.

a. Stepwise control experiment.

b. Stepwise main experiment.

The vertical lines show when the power was switched off for reaching the temperature given.

c. Continuous main experiment.

The vertical lines correspond to the moments when the given temperature values were reached as indicated by the Helipot potentiometer R16 (Fig. 4).

In the stepwise experiment (b) the curve follows a very characteristic pattern. When the power is switched on, the recorded temperature of the water-containing bomb (as measured in the wall) rises more rapidly than that of the bomb holding the peat suspension. As soon as the power is switched off, the temperature difference decreases, changes sign, and levels off close to the zero-line. Thereupon, additional energy is supplied to the coolest (water-containing) bomb until equilibrium is attained at zero temperature difference. The ΔT -peaks decrease in size as the temperature of the system increases.

The explanation for this behaviour is very simple - the heat conductivity of the native peat suspension is significantly less than that of the water, which is mainly due to the higher viscosity of the suspension. Therefore, when the power is switched on, the temperature gradient built up in the peat-containing bomb will be higher than that in the water system and a temperature difference will be recorded between the walls of the two bombs. As soon as the power is switched off, equilibrium will be attained within the bombs and ΔT diminishes. An apparent exothermicity of the peat system results in a change of sign of ΔT . The decrease in size of the ΔT -peaks is explained by the fact that structural and chemical changes which the peat undergoes when the temperature increases, result in a strong decrease in viscosity and thus an increase in heat conductivity of the suspension. The wet-carbonized peat suspension has almost the same viscosity as water. The given explanation is strengthened by the results from experiments performed, substituting wet-carbonized for native peat suspension. In this case the ΔT -curve was found to be almost identical to that in the control experiments using water in both bombs. On the other hand, experiments in which wet-carbonized peat had been substituted for water gave the type b and c curves.

The curve from the continuous heating experiment (c) starts out similar to the b-curve. However, at ca. 50°C it passes a maximum and begins to fall off, reverses sign, and levels off at a value indicating an appreciable apparent exothermal reaction. The above explanation also holds in this case, remembering, that the build-up of an internal temperature gradient in the peat-suspension will increase the heat conduction towards the wall of the bomb, that the viscosity decreases rapidly with increasing temperature, and that the wet-carbonizing process occurs under an apparent production of heat.

Heat equivalent measurements

The very broad temperature interval under which measurements were performed together with the presence of a gas phase in the bomb accounts for the fact that the heat equivalent of the bomb increased by a factor of 3 between room temperature and 220°C. The amount of water which vaporizes per degree increases continuously when the temperature rises and the corresponding energy of vaporization constitutes an essential part of the heat equivalent. Therefore, it had to be determined at several temperatures and a curve had to be constructed from which the value of the heat equivalent could be obtained at any arbitrary temperature.

The heat equivalent of the water-filled bombs was determined by adding a known amount of electrical energy to one of them starting at varying temperatures from 20° to 220°C , and measuring the resulting temperature difference.

The energy supplied was calculated from the voltage drop across the heater, its resistance, and the duration of the heating period. The resistance of the heaters varied slightly with temperature; the variation was measured in separate experiments and a corresponding small correction was applied.

CALCULATION OF RESULTS

Principally, the calculation of the results for an experiment performed in an ideal adiabatic twin calorimeter system is very simple. The heat evolution in one of the bombs is precisely balanced by an input of a known amount of electrical energy in the other. For a number of reasons it is not so in practice: (a) the amount of electrical energy generated in the two heaters during warm-up may not be identical, (b) the heat equivalent of the two empty bombs may not be the same, (c) the calorimetric system may not be truly adiabatic and (d) the chemical and thermal properties of the contents of the two bombs are definitely dissimilar.

By comparing the results from a control experiment (with the same amount of water in the two bombs) with those from a main experiment, the errors due to the effects (a) and (b) will cancel completely. The effect (c) will be separately treated under "Heat exchange corrections" while (d) will be considered in calculating the true heat of wet-carbonization from the primary experimental results.

Heat exchange corrections

During the rapid warm-up of the two bombs and the surrounding thermostat it is unavoidable that, temporarily, certain temperature differences will build up. Those existing between the air thermostat and the total calorimeter system may be neglected as they will cause equal effects on the two bombs. However, the difference in temperature between the two bomb surfaces will cause a heat exchange, which has to be corrected for. The position of the platinum resistance thermometer is such that it very nearly will measure the temperature of the wall of the bomb, that is, the temperature that governs the heat exchange with the surroundings.

If we assume, that the heat flow dw/dt follows Newton's equation, then

$$dw = k(T_c - T_s) dt \quad (7)$$

where T_c and T_s are the temperatures of the bomb surface and the surroundings, respectively, and k is a constant equal to the heat flow for $T_c - T_s = 1^\circ$.

Hence, for the two bombs we have

$$dw' = k(T'_c - T_s) dt \text{ and } dw'' = k(T''_c - T_s) dt$$

The quantity which has to be corrected for, however, is

$$d\Delta w = dw' - dw'' = k(T'_c - T''_c) dt = k \cdot \Delta T \cdot dt \quad (8)$$

But

$$\frac{d\Delta w}{dt} = \frac{d\Delta T}{dt} \cdot E \quad (9)$$

where E is the energy equivalent of the bomb.

Hence

$$d\Delta T \cdot E = k \cdot \Delta T \cdot dt \quad (10)$$

and the total correction for the heat exchange will be

$$\Delta T_{\text{corr}} = \int d\Delta T = \int \frac{k}{E} \cdot \Delta T \cdot dt \quad (11)$$

In separate experiments performed at a number of temperatures from 20° to 220°C, k was found to be constant at each temperature and thus independent of the value of ΔT . (The value of k increases slightly with temperature).

The heat exchange correction was obtained in the conventional way by graphical integration of the recorded ΔT -curve⁹ (Figure 6). In no case did the correction exceed 10 % of the excess input of electrical energy.

MATERIALS

In the present investigation four types of peat of different biological origin and degree of humification have been used. All samples were taken from Förrarps peat-bog near Ljungby in Southern Sweden. A 50-liter master sample was prepared by finely grinding the peat and part of this sample was diluted with water to ca. 4 % dry weight. The samples are characterized in Table 1.

Table 1.
Characterization of the peat samples.

No.	Origin of peat	Degree of humification*)	Dry weight %
1	Sphagnum	2 - 3	4.80
2	Sphagnum	3 - 4	4.21
3	Sphagnum peat + some Thelypteris peat	7 - 8	4.28
4	Sedge peat + some Sphagnum and Phragmites peat	7	4.07

*) The degree of humification is enumerated from 1 to 10, a low value indicates a low degree of humification. (Cf. Ref. ¹⁰).

CALORIMETRIC RESULTS

Tables 2 to 5 give the amounts of excess energy added to the water-filled bomb to bring it up to the same final temperature as that of the bomb containing the peat suspension. The results are expressed in kcal per kg peat, d. wt., and have been corrected to hold good for the temperature intervals given. All corrections listed above, have been incorporated.

The agreement in the results of the continuous and the stepwise experiments is satisfactory and within the expected limits of error. ^{*)} This indicates that systematic errors of different magnitude in the two series of experiments are not present and that the final states are identical.

It has thus been demonstrated, that, under given conditions, the energy required for heating an amount of peat suspension, corresponding to 1 kg of peat d. wt., from 20 to 220°C, is between 125 and 175 kcal less than the energy required for heating the same mass of water. ^{**)} A trend in this direction is of course to be expected, as the specific heat of the peat substance is considerably less than that of the same amount of water. However, if due allowance is made for this fact, the results clearly indicate that some exothermal process occur above ca. 160°C.

Tables 2 - 5.

Results of the calorimetric experiments.

The numbers given, Q, represent the corrected excess energy in kcal per kg peat d. wt. that was added to the reference (water-filled) calorimeter can in order to increase its temperature to that of the native peat calorimeter can.

^{*)} The standard deviation of a weighed mean from all 22 experiments was found to be $\pm 0.02\%$ as counted on the total amount of supplied energy.

^{**)} It will later be shown, that the energies used up for the evaporation of water in the two bombs, are almost equal.

Table 2, Peat No. 1.

Run no. Temp. interval	Continuous heating			Step-wise heating			Mean
	11	12	13	14	15	16	
20 - 40				11	12	12	12
40 - 70				14	16	14	15
70 - 100				15	14	15	15
100 - 130				12	19	19	17
130 - 160				17	18	19	18
160 - 190				24	23	23	23
190 - 220				49	47	60	52
Sum	176	126	139	142	149	162	152
Average result	147			151			
Mean	149 [±] 7* kcal/kg peat d. wt.						

Table 3, Peat No. 2.

<div>Run no.</div> <div>Temp. interval</div>	Step-wise heating			Continuous heating		Mean
	22	23	24	25	26	
20 - 40	9	8	4			7
40 - 70	13	11	18			14
70 - 100	11	8	16			12
100 - 130	13	17	11			14
130 - 160	15	10	15			13
160 - 190	30	15	22			22
190 - 220	45	46	40			44
Sum	136	115	126	131	120	126
Average result	126			126		
Mean	126 \pm 4 kcal/kg peat d. wt.					

*) standard deviation of the mean.

Table 4, Peat No. 3.

<div>Run no.</div> <div>Temp. interval</div>	Continuous heating			Step-wise heating			Mean
	41	42	43	44	45	46	
20 - 40				7	4	10	7
40 - 70				23	24	15	21
70 - 100				17	13	13	14
100 - 130				19	16	22	19
130 - 160				25	25	18	23
160 - 190				35	32	29	32
190 - 220				46	49	46	47
Sum	179	176	190	172	163	153	163
Average result	182			163			
Mean	173 ⁺ 5 kcal/kg peat d. wt.						

Table 5, Peat No. 4

Run no. Temp. interval	Continuous heating			Step-wise heating			Mean
	51	52	53	54	55	56	
20 - 40				6		10	8
40 - 70				17		16	17
70 - 100				8		10	9
100 - 130				8		8	8
130 - 160				8		16	12
160 - 190				23		29	26
190 - 220				38		45	42
Sum	142	135	119	108		134	122
Average result	132			121			
Mean	127 \pm 6 kcal/kg peat d. wt.						

ESTIMATION OF THE ENTHALPY CHANGE

As was explained above (p. 5) it is not possible to calculate rigorously the exothermicities of the chemical changes occurring during the wet-carbonization process. However, it is of considerable interest to make an estimate of them so that the present results can be compared with those obtained in previous investigations.

In order to estimate the changes in enthalpy, ΔH , from the data given in Tables 2 to 5, the differences between the thermal behaviour of the water and the peat suspension have to be considered (cf. above).

- a. The heat capacities of the peat and its decomposition products are different from that of water.
- b. The formation of soluble products during the wet-carbonization process lowers the water vapor pressure.
- c. The formation of carbon dioxide from the peat gives rise to several effects, like heat of solution, changes in vapor pressure etc.
- d. As the experiments were performed at constant volume, the change in internal energy, ΔE , was measured. In order to arrive at the corresponding values of the heat of reaction occurring at constant pressure, the enthalpy values, ΔH , the heat of expansion of the carbon dioxide must be taken into account.

The influence of the varying heat capacity of peat and its decomposition products.

No value of the heat capacity of native peat could be found in the literature. Therefore, it was determined calorimetrically (calorimeter D, Ref. ¹¹), at 25°C on a 6,6% peat suspension. The average value found was $c = 0,35 \pm 0,04 \text{ cal} \cdot \text{g}^{-1} \cdot \text{deg}^{-1}$. The temperature coefficient of c was taken to be equal to that of cellulose and related substances i.e. + 0.001 in the temperature interval 0 to 100°C. (Ref. ⁶). Assuming the same coefficient to be valid also above 100°C, the specific heat of peat may be expressed as (t in °C):

$$c_t = 0.32 + 0.001 t \quad (12)$$

At temperatures above ca. 150°C the peat substance starts to decompose under the formation of essentially carbonized peat, water, carbon dioxide and water soluble low molecular weight products, like formic acid, acetic acid and carbohydrates.

The approximate amounts of carbon dioxide and water soluble products formed, as a function of temperature, are shown in Figure 7 (Ref. ¹²). The heat capacity of the

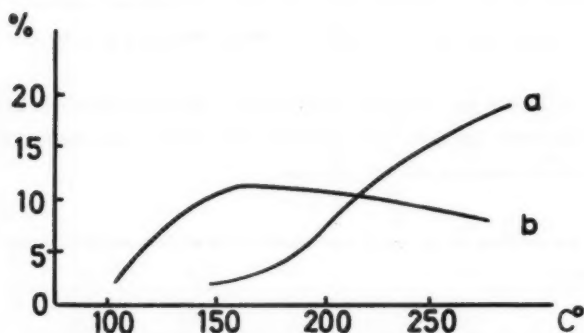


Figure 7

The approximate amounts of carbon dioxide (a) and water-soluble products (b) found during the wet-carbonization process as a function of reaction temperature (from Ref. ⁷).

carbonized peat has been taken equal to that of charcoal, 0.3 at 25°C. For water, the carboxylic acids and carbohydrates, values of the specific heat have been taken from the literature ¹³. For carbon dioxide ¹⁴ c_v -values between 0.16 and 0.19 have been used in the interval 100 to 220°C.

The apparent values of the specific heat of the peat (and its decomposition products) are then calculated to 0.42 cal · g⁻¹ · deg⁻¹ between 100 and 130°C, 0.45 between 130 and 160, 0.49 between 160 and 190, and 0.55 between 190 and 220°C. Within the overall uncertainty the values are identical to those obtained with the use of equation (12).

The difference between the heat capacity of water and that of peat and its decomposition products in the appropriate temperature intervals constitutes the main correction term for calculating the ΔE -values from the results given in Tables 2 to 5. As an example, in the interval 160 to 190°C this correction amounts to (1.01-0.49) · 30 = 15.6 kcal per kg of peat d. wt.

The influence of the formation of water-soluble products.

The presence of water soluble products decreases the water vapor pressure. The depression can be estimated by using Raoult's law, the concentration of soluble products needs then to be known. Assuming a 10 % conversion of the native peat into soluble products and an average molecular weight of the active species of 50, the maximum concentration will be $0.1 \text{ mole} \cdot \text{liter}^{-1}$. The depression of the equilibrium pressure is then at 220°C ca. 0.2 % or 0.04 atm. The volume of the gas phase in the bomb is 0.2 l. from which the amount of water which does not vaporize due to the presence of the soluble products is calculated to be 2×10^{-4} mole. The heat of vaporization of this amount at 220°C is only ca. 2 cal and thus insignificant.

The influence of the presence of carbon dioxide.

The CO_2 interferes in several ways with the thermal measurement:

- a. It is distributed between the liquid and the gaseous phases and the distribution is temperature dependent. The heat of solution is ca. 0.1 kcal per gram of CO_2 at room-temperature and is also expected to vary with temperature.
- b. Its pressure in the gas phase increases the water vapor pressure¹⁵
- c. It lowers the heat of vaporization of water¹⁵.

Experimental data seemed not to be available from which the heat effects could be estimated with any confidence. A few experiments were therefore undertaken to determine the approximate gross heat effect between 20 and 220°C . The bombs were filled with pure water and to one of them were added ca. 1.6 grams of dry ice. The bomb was closed as rapidly as possible, weighed, and an ordinary run performed in the temperature intervals 20-100, 100-150, and 150- 220°C .

The average result from a series of three determinations indicated that the apparent specific heat of the carbon dioxide was negative - a mean value of $-0.6 \pm 0.3 \text{ cal} \cdot \text{g}^{-1} \cdot \text{deg}^{-1}$ was obtained instead of the value of +0.2 used above. Thus, the correction which has to be applied in the appropriate temperature interval, 160 to 220°C , is 5 kcal per kg peat d.wt. and it has to be subtracted from the exothermicity values. Between 160 and 190°C the correction has been put equal to 2 and between 190 and 220°C to 3 kcal per kg of peat d.wt.

The result from the application of the mentioned corrections a to d to the values in Tables 2 to 5 are given in Tables 6 to 9. The standard convention has been used, i.e. a positive $-\Delta H$ -value means an exothermal process.

Tables 6 - 9

Heat of wet-carbonization of peat, $-\Delta H$, in kcal per kg peat d. wt.

Table 6, Peat No. 1.

<div>Run. no.</div> <div>Temp. interval</div>	Continuous heating			Step-wise heating			Mean
	11	12	13	14	15	16	
20 - 40				-2	-1	-1	-1
40 - 70				-5	-3	-5	-4
70 - 100				-3	-4	-3	-3
100 - 130				-4	3	3	1
130 - 160				0	1	2	2
160 - 190				6	5	5	5
190 - 220				30	28	41	33
Sum	56	6	19	22	29	42	33
Average result	27			31			
Mean	29 \pm 7 kcal/kg peat d. wt.						

Table 7, Peat No. 2.

<div>Run no.</div> <div>Temp. interval</div>	Step-wise heating			Continuous heating		Mean
	22	23	24	25	26	
20 - 40	-4	-5	-9			-6
40 - 70	-6	-8	-1			-5
70 - 100	-7	-10	-2			-6
100 - 130	-3	1	-5			-2
130 - 160	-2	-7	-2			-4
160 - 190	12	-3	4			4
190 - 220	26	27	21			25
Sum	16	-5	6	11	0	6
Average result	6			6		
Mean	6 ± 4 kcal/kg peat d. wt.					

Table 8, Peat No. 3

<div>Run no.</div> <div>Temp interval</div>	Continuous heating			Step-wise heating			Mean
	41	42	43	44	45	46	
20 - 40				-6	-9	-3	-6
40 - 70				4	5	-4	2
70 - 100				-1	-5	-5	-4
100 - 130				3	0	6	3
130 - 160				8	8	1	6
160 - 190				17	14	11	14
190 - 220				27	30	27	28
Sum	59	56	70	52	43	33	43
Average result	62			43			
Mean	53 ⁺ 5 kcal/kg peat d. wt.						

Table 9, Peat No. 4.

Run no. Temp. interval	Continuous heating			Step-wise heating			Mean
	51	52	53	54	55	56	
20 - 40				-7		-3	-5
40 - 70				-2		-3	-3
70 - 100				-10		-8	-9
100 - 130				-8		-8	-8
130 - 160				-9		-1	-5
160 - 190				5		11	8
190 - 220				19		26	23
Sum	22	15	-1	-12		14	1
Average result	12			1			
Mean	7 ± 6 kcal/kg peat d. wt.						

DISCUSSION OF RESULTS

Comparison with earlier measurements.

The obtained $-\Delta H$ -values show a considerable spread. However, it has to be considered that the results appear as small differences between large numbers - the total amount of energy required to heat the peat suspension under the conditions of the experiment from 20 to 220°C is ca. 20 000 kcal per kg of peat d.wt. It may therefore be concluded that the reproducibility of the measurements is satisfactory. Systematic errors cannot be excluded particularly in the heat capacity estimation, and these errors are estimated to ca. 6 kcal per kg of peat d.wt. in the ΔH -value for the whole temperature interval.

From the results it is apparent that an obvious correlation does not exist between the degree of humification or the biological origin and the exothermicity of the process. Besides, the experimental material is far too small to allow any general conclusions of that kind to be drawn. However, it is evident that the wet-carbonization is only slightly exothermal, contrary to what has been reported previously by Odén^{2,3}, Terres^{4,5} and Lundén and Cederquist⁶.

A study of the ΔH -values from the stepwise experiments shows the same overall picture for the four types of peat investigated: At low temperatures (0 to 100°C) an endothermal effect is prevailing, as the temperature rises above 100°C, the effect changes sign somewhere in the interval 100 to 190°C. Finally, above 190°C, the effect is definitely exothermal. It is interesting to note that the amount of heat evolved during the last step between 190 and 220°C is, within the limits of error, the same in the four cases.

A comparison between the present results and those of Lundén and Cederquist⁶ shows a striking difference. These authors, who studied the wet-carbonization process between 20 and 185°C, found rather high exothermicity values, varying between 50 and 150 kcal per kg of peat d.wt.^{*)} The discrepancy is more pronounced when it is considered, that L. and C. report the exothermal effects to occur only in the interval 70 to 140°C. Further, the authors found that peat of a low degree of humification showed a large exothermal effect, whereas the highly humified sample showed a comparatively small effect.

*) For the purpose of comparison the results of L. and C. are those given for total peat substance, i.e. including ashes.

These apparent differences in result may be traced back to the different methods used in the two investigations. Lundén and Cederquist worked with essentially an adiabatic one-bomb system and carried out two consecutive runs, without opening the bomb between the experiments. The first run was performed on the native peat suspension, the second was a comparison run with the carbonized peat suspension in the bomb. At a constant supply of electrical energy, two temperature - time curves were obtained, the difference between which, multiplied by the heat equivalent of the system, was considered to give directly the exothermicity of the process.

The specific heat of the sum of products of reaction was put equal to that of the native peat substance - an assumption which was shown above to be well justified. In the comparison experiment, however, carbon dioxide was present from the start of the run. To a certain extent the gas is dissolved in the liquid phase and upon heating some of it is transferred to the gas phase. The heat of solution of carbon dioxide is ca. 0.1 kcal per g of CO_2 , and is exothermal. An additional amount of energy has therefore to be supplied to the carbonized peat suspension, i.e. to the comparison experiment, to compensate for the endothermal transfer of CO_2 . Under the experimental conditions, the temperature rise in the comparison experiment will therefore lag behind that of the main experiment, which will be interpreted as an exothermal effect during the early stage of the wet-carbonization process. However, an estimation of the expected error from this source showed that it could hardly account for more than 10 kcal difference. The cause of the discrepancy must therefore be sought elsewhere.

One distinct difference between the measurements of L. and C. and the present ones is the rate of heating. The duration of L. and C.'s experiments was ca. 180 minutes, whereas in the present case the duration of the continuous and the stepwise runs was ca. 30 and 130 minutes, respectively. L. and C. observed that somewhat higher exothermicity values were obtained at a lower rate of heating. Although this trend could be interpreted by assuming that the reactions occurring are not completed within their normal heating period, no support of this explanation is given by the results of the present investigation. On the contrary, we do find an agreement between the continuous and the stepwise runs, although the time effect should be more pronounced when the duration of the experiments varies in the ratio 1 to 4. Also, no heat effect was observed in the continuous experiment when the temperature of the system was followed for some length of time after the final temperature, 220°C , had been reached. Therefore, a varying length of the heating period cannot possibly account for the existing discrepancy.

The following explanation for the disagreement is tentatively suggested. The manually or automatically operated control of adiabacy is governed by the difference in temperature of the calorimeter-bomb and the surrounding jacket as measured with some thermometers placed in the bomb and in the jacket, respectively. On the other hand, the heat exchange depends on the temperature difference between the outer surface of the bomb and the inner surface of the jacket. It is therefore of utmost importance that the temperature measuring devices indicate as nearly as possible the surface temperatures. It was mentioned previously, that in our early experiments in which the thermometer well was placed inside the body of the bomb and thus fairly close to the heater, the measured temperature could easily be up to 10°C higher than that of the bomb surface (heating rate 5° per min.). This made it necessary to incorporate the thermometer well into the wall of the bomb as well as to change the construction material from stainless steel to brass. Before these precautions had been taken, the results obtained were seriously wrong due to the application of erroneous heat exchange corrections made under the assumption that the measured temperature of the bomb was that of its surface. It was found that the error was particularly significant at low temperatures and this was explained as caused by the high viscosity of the native peat suspension (cf. p. 15). The thermometer wells in the stainless steel calorimeter of Lundén and Cederquist are located inside the body of the bomb and between the heaters. They therefore measure the temperature of the peat suspension and not that of the outer surface. This is somewhat cooler than the interior parts of the bomb. It is particularly so in the main experiment at fairly low temperatures, when the high viscosity (that is low heat conductivity) of the liquid phase slows down the heat transfer to the wall of the bomb. The heating of the surrounding jacket is therefore adjusted to a temperature which is higher than that of the surface of the bomb. Instead of having adiabatic conditions, energy flows from the jacket to the bomb and the flow is more pronounced in the main run than in the comparison run, as the viscosity of the carbonized peat suspension is almost as low as that of water.

Moreover, as the viscosity of a peat of low-degree of humification is higher than that of a high degree, it is to be expected that the apparent exothermicity values, as found in the experiments of L. and C., should decrease in the order low-high humified peat.

The finding of L. and C. that the apparent exothermal effect does not start until 60°C is difficult to bring into accordance with the explanation given here. One should expect the effect to show up at an earlier stage. However, a simultaneously occurring endothermal effect as indicated by the present investigation might partly obscure the picture.

The indirect determinations by Odén², Odén and Unnerstad³ and Terres⁴ have given much higher values of the heat of wet-carbonization of peat than the direct calorimeter measurements. Odén determined the heat of combustion of native peat and that of the corresponding carbonized peat (apparently Terres did the same, but no experimental data are given). From the values of the heat of combustion and the ratio between the amount of dry substance before and after the wet-carbonization process, exothermicity was calculated. It is not surprising that the results came out very high, as no consideration was given to the heat of combustion of the water-soluble and the volatile reaction products. Odén and Unnerstad analyzed the reaction solution for water soluble, non-volatile products and corrected for their heats of combustion. The authors still obtained high values, ca. 1000 kcal per kg of peat d.wt., probably because products like formic and acetic acid and furfural were not accounted for. Besides, the duration of the wet-carbonization experiment was as long as ca. 10 hours.

The chemistry of the wet-carbonization process.

Very little is known about the chemistry of the wet-carbonization process. A few authors have expressed certain views about possible types of reactions and related heat effects.

Terres⁴ and Terres and Schultze⁵ discuss to some length the interesting question of the chemical and physical changes behind the thermal effects. The authors assume that the "destruction of the colloidal state" is endothermal whereas the decarboxylation and dehydration reactions are supposed to be exothermal. The former process should occur spontaneously at a certain temperature, but the degradation reactions were supposed to be rather slow.

The conclusions of the authors were based on observations of time - temperature curves when heating peat and water, respectively, in an autoclave. T. and S. found apparent endothermal effects between 0° and 95°C but interpreted these properly as due to poor heat conductivity in the native peat suspension as compared to that of water. From 95°C, a rather sudden change in the temperature curve of the native peat experiment occurred, formally indicating a strong exothermal process. This explanation was also given by the authors and related to decarboxylation and dehydration reactions. The influence of the changing viscosity was not considered at all.

It is apparent from what has been said previously that the results from measurements of this kind cannot be explained in a simple way. In addition to this, Terres and Schultze used the same amount of ca. 10 % peat suspension and water in their experiments without correcting for the appreciable difference in specific heat.

It is thus doubtful, if the experimental technique used by T. and S. allows any firm conclusion relating possible chemical and physical changes to the thermal effect. The statement, that the decarboxylation process should be exothermal is contrary to all thermochemical evidence - all simple decarboxylation reactions are endothermal. An ordinary dehydration reaction is usually slightly either exothermal or endothermal. However, a simultaneous occurrence of condensation reactions leading to i.a. fused, aromatic ring systems could give an appreciable exothermicity.

Already Odén pointed out that the removal of hydroxyl groups from the native peat under formation of water and water-soluble products ought to make the peat more hydrophobic, that is, easier to free from "colloidally bound" water. The same statement should also be valid for the removal of carbon dioxide. Terres and Schultze⁵ assume that the "destruction of the colloidal state" is independent of and often foregoes the decarboxylation and dehydration reactions, an assumption which can be very much doubted.

ACKNOWLEDGEMENTS

This investigation was suggested to us by the Research Laboratory of The Swedish Peat Company, who encouragingly supported the project both technically and financially in a very generous way.

The skillful help of Mr. T. Hedetoft, who carried out most of the experimental work, is gratefully acknowledged.

SUMMARY

A quasi-adiabatic twin-calorimeter was developed and used for the determination of heat effects accompanying the wet-carbonization of peat as studied in the temperature interval 20 to 220°C. The calorimeter had incorporated some rather unique features: the rate of heating was very high or ca. 7°C per minute, the working pressure was ca. 30 atm. and the reproducibility was very satisfactory - the standard deviation of the 22 measurements was found to be $\pm 0.02\%$ counted on the total amount of supplied energy.

The direct calorimetric results showed that the amount of electrical energy necessary to heat a quantity of a 4 % peat suspension containing 1 kg of peat, dry weight from 20 to 220°C was 125 to 175 kcal less than that used up by the same mass of water. From these results the negative value of the enthalpy change (= exothermicity) accompanying the wet-carbonization under conditions given above was estimated to be rather low, between 50 and almost 0 kcal per kg of peat, dry weight.

The present results are discussed in comparison to previous measurements.

REFERENCES

1. C. B. Vignoles, Irish Pat. No. 782, 1850
2. S. Odén, Tekn. Tidskr. Kemi och Bergsvetenskap 50 (1920) 59
3. S. Odén, A. Unnerstad, Brennstoff-Chemie 5 (1924) 249
4. E. Terres, Brennstoff-Chemie 33 (1952) 1
5. E. Terres, K. Schultze, Brennstoff-Chemie 33 (1952) 353
6. B. Lundén, K. N. Cederquist, Proceedings IVA 23 (1952) 203
7. T. Widell, IVA 18 (1947) 178. See also
T. Widell, W. Teichert, Torvlaboratoriets Medd. No. 7, 15.2.1949
8. R. Norin, Geol. Fören., Stockholm, Förhandl. 63 (1941) 203
9. F. D. Rossini, Editor, Experimental Thermochemistry, Interscience Publ., Inc., New York 1956
10. According to The Geological Survey of Sweden
11. S. Sunner, I. Wadsö, Acta Chem. Scand. 13 (1959) 97
12. Research Laboratory of the Swedish Peat Company, Unpublished results
13. Handbook of Chemistry and Physics, 39th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio
14. Int. Crit. Tables, Vol. 5, p. 83, McGraw Hill Comp., New York 1929
15. F. Pollitzer, E. Streberl, Z. Phys. Chem. 110 (1924) 768





THE LAST VOLUMES OF ACTA POLYTECHNICA

Chemistry including Metallurgy Series

(The predecessor of Acta Polytechnica Scandinavica)

Volume 4

- Nr 10 BJÖRKMAN, L, BJÖRKMAN, M, BRESKY, A, ENEBO, L, and RENNERFELT, J: *Experiments on the Culture of Chlorella for Food Purposes*. Acta P 176 (1955), 18 pp, Sw. Kr 4: 00
UDC 663.11:582.2
- Nr 11 WRANGLÉN, G: *Dendrites and Growth Layers in the Electrocrystallization of Metals*. Acta P 182 (1955), 42 pp, Sw. Kr 6: 50
UDC 669.017:548.232.4:669.017:548.52
- Nr 12 MATTSSON, E: *The Electrode Process in Metal Deposition from Aqueous Solutions*. Acta P 184 (1955), 56 pp, Sw. Kr 6: 50
UDC 541.135:621.357
- Nr 13 EDHBOG, A: *Studies on a Water-Soluble Material from the Masonite Process*. Acta P 197 (1956), 87 pp, Sw. Kr 12: 50
UDC 547.454:542.938:542.941
out of print

ACTA POLYTECHNICA SCANDINAVICA

Chemistry including Metallurgy Series

- Ch 1 JART, A: *Fat Rancidity. Summaries of Papers Presented at the 2nd Scandinavian Symposium on Fat Rancidity*. (Acta P 242/1958) 72 pp, Sw. Kr 7: 00
UDC 665.112.2
- Ch 2 ERÄMETSÄ, O: *Ion Characteristics: a New Way of Assessing the Chemical Properties of Ions*. (Acta P 249/1958) 22 pp, Sw. Kr 7: 00
UDC 541.7
- Ch 3 ERÄMETSÄ, O: *On the Decomposition of Polish Felspar*. (Acta P 260/1959) 17 pp, Sw. Kr 7: 00
UDC 553.61:542.92
- Ch 4 Report of the Committee on Slaughtering Methods Appointed by the Danish Academy of Technical Sciences at the Request of the Ministry of Justice. (Acta P 264/1959) 35 pp, Sw. Kr 7: 00
UDC 637.513.22
- Ch 5 MÄKIPIRTTI, S: *On the Sintering of W-Ni-Cu Heavy Metal*. (Acta P 265/1959) 69 pp, Sw. Kr 7: 00
UDC 621.762:669.275.24.3
- Ch 6 PAULSEN, A: *Constitution des Quatre Isomeres de Position des Chloro et Aminomethylbenzodioxannes-1,4, Substitues dans le Noyau Benzenique*. (Acta P 270/1960) 94 pp, Sw. Kr 7: 00
UDC 547.84:615.45
- Ch 7 DAHLGREN, S-E: *Physico-Chemical Background of Phosphoric Acid Manufacture by Wet Processes*. (Acta P 271/1960) 15 pp, Sw. Kr 7: 00
UDC 661.634
- Ch 8 SUNDIUS, N: *Felspar and its Influence on the Reactions in Ceramics during Burning*. (Acta P. 272/1960), 29 pp, Sw. Kr. 7: 00
UDC 666.6.041.9:553.61
- Ch 9 DAHL, OLE: *Gamma Irradiation of Vacuum-Packed Sliced Meat Products*. (Acta P. 276/1960), 24 pp, Sw. Kr. 7: 00
UDC 664.91.037:539.166
- Ch 10 ENEBO, LENNART AND PEHRSON, STIG O: *Thermophilic Digestion of a Mixture of Domestic Sewage Sludge and Cellulose Materials*. (Acta P. 281/1960) 40 pp, Sw. Kr. 7: 00
UDC 663.1:628.35:676.16
- Ch 11 ASCHAN, L. J.: *Studies on the ternary system Cu-Mg-Si*. (Acta P. 285/1960) 46 pp, Sw. Kr. 7: 00
UDC 669.018.669.3.721.782 (084.2)
- Ch 12 ERÄMETSÄ, OLAVI and KOLEHMAINEN, ANTTI: *A Modification of the Ion Characteristic to the Glass Theory and the Glasses Coloured with Lanthanons*. (Acta P. 290/1960). 22 pp. Sw. Kr. 7:00
UDC 666.24.01:546.65
- Ch 13 ALERTSEN, AASE RYE: *Ageratochromene, a Heterocyclic Compound from the Essential Oil of Ageratum houstonianum Mill.* (Acta P. 293/1961). 66 pp. Sw. Kr. 7:00
UDC 547.81:547.913
- Ch 14 SUNNER P, S. and WADSÖ, I: *Measurements of Heat Effects accompanying the wet Carbonization of Peat in the Temperature Range 20 to 220 Degrees C.* (Acta P. 297/1961). 40 pp Sw. Kr. 7:00
UDC 536.662:662.641

Price Sw. Kr. 7:—

